



(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
07.05.2003 Bulletin 2003/19

(51) Int Cl.7: **C10G 9/14, C10G 9/00**

(21) Application number: 00119326.7

(22) Date of filing: 22.03.1996

(54) **Method for providing a tube having carbon monoxide inhibiting properties when used for the thermal cracking of hydrocarbons**

Verfahren zur Versorgung eines Rohres mit Kohlenmonoxidhemmenden Eigenschaften beim thermischen Cracken von Kohlenwasserstoffen

Méthode pour fournir un tube ayant des propriétés d'inhibiteur de formation de monoxyde de carbone lorsqu'utilisé dans le craquage d'hydrocarbures

(84) Designated Contracting States:
AT BE DE ES FR GB IT NL SE

(30) Priority: 23.03.1995 US 409292

(43) Date of publication of application:
22.11.2000 Bulletin 2000/47

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
96104603.4 / 0 733 693

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EP 1 054 050 B1

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Description

[0001] The present invention generally relates to processes for the thermal cracking of hydrocarbons and, specifically, to a method for providing a tube of a thermal cracking furnace having carbon monoxide production inhibiting properties when used for the thermal cracking of hydrocarbons.

[0002] In a process for producing an olefin compound, a fluid stream containing a saturated hydrocarbon such as ethane, propane, butane, pentane, naphtha, or mixtures of two or more thereof is fed into a thermal (or pyrolytic) cracking furnace. A diluent fluid such as steam is usually combined with the hydrocarbon feed material being introduced into the cracking furnace.

[0003] Within the furnace, the saturated hydrocarbon is converted into an olefinic compound. For example, an ethane stream introduced into the cracking furnace is converted into ethylene and appreciable amounts of other hydrocarbons. A propane stream introduced into the furnace is converted to ethylene and propylene, and appreciable amounts of other hydrocarbons. Similarly, a mixture of saturated hydrocarbons containing ethane, propane, butane, pentane and naphtha is converted to a mixture of olefinic compounds containing ethylene, propylene, butenes, pentenes, and naphthalene. Olefinic compounds are an important class of industrial chemicals. For example, ethylene is a monomer or comonomer for making polyethylene. Other uses of olefinic compounds are well known to those skilled in the art.

[0004] As a result of the thermal cracking of a hydrocarbon, the cracked product stream can also contain appreciable quantities of pyrolytic products other than the olefinic compounds including, for example, carbon monoxide. It is undesirable to have an excessively high concentration of carbon monoxide in a cracked product stream; because, it can cause the olefinic product to be "off-spec" due to such concentration. Thus, it is desirable and important to maintain the concentration of carbon monoxide in a cracked product stream as low as possible.

[0005] Another problem encountered in thermal cracking operations is in the formation and laydown of carbon or coke upon the tube and equipment surfaces of a thermal cracking furnace. This buildup of coke on the surfaces of the cracking furnace tubes can result in an excessive pressure drop across such tubes thereby necessitating costly furnace shutdown in order to decoke or to remove the coke buildup. Therefore, any reduction in the rate of coke formation and coke buildup is desirable in that it increases the run length of a cracking furnace between decokings.

[0006] It is thus an object of this invention to provide an improved process for cracking saturated hydrocarbons to produce olefinic end-products.

[0007] Another object of this invention is to provide a process for reducing the formation of carbon monoxide in a process for cracking saturated hydrocarbons.

[0008] A still further object of this invention is to improve the economic efficiency of operating a cracking process for cracking saturated hydrocarbons by providing a method for treating the tubes of a cracking furnace so as to provide treated tubes having carbon monoxide production inhibiting properties.

[0009] In accordance with the invention a method for reducing a concentration of carbon monoxide present in a cracked gas stream produced by passing a hydrocarbon stream through a tube of a thermal cracking furnace, as defined in claim 1, is provided. This method includes treating the tubes of the thermal cracking furnace by contacting it with a hydrogen gas containing a sulfur compound thereby providing a treated tube having properties which inhibit the production of carbon monoxide during the thermal cracking of hydrocarbons. The hydrocarbon stream is passed through the treated tubes while maintaining the treated tubes under suitable cracking conditions to thereby produce a cracked gas stream having a reduced concentration of carbon monoxide below the concentration of carbon monoxide that would be present in a cracked gas stream produced by an untreated tube.

[0010] In the accompanying drawing:

FIG. 1 provides a schematic representation of the cracking furnace section of a pyrolytic cracking process system in which the tubes of such system are treated by the novel method described herein. FIG. 2 is a plot of the weight percent of carbon monoxide in a cracked gas stream versus the time of on-line cracker operation for tubes treated in accordance with the method according to the invention described herein and for conventionally treated tubes.

[0011] Other objects and advantages of the invention will be apparent from the following detailed description of the invention and the appended claims thereof.

[0012] The process of this invention involves the pyrolytic cracking of hydrocarbons to produce desirable hydrocarbon end-products. A hydrocarbon stream is fed or charged to pyrolytic cracking furnace means wherein the hydrocarbon stream is subjected to a severe, high-temperature environment to produce cracked gases. The hydrocarbon stream can comprise any type of hydrocarbon that is suitable for pyrolytic cracking to olefin compounds. Preferably, however, the hydrocarbon stream can comprise paraffin hydrocarbons selected from the group consisting of ethane, propane, butane, pentane, naphtha, and mixtures of any two or more thereof. Naphtha can generally be described as a complex hydrocarbon mixture having a boiling range of from 82 to 204°C (180°F to 400°F) as determined by the standard testing methods of the American Society of Testing Materials (ASTM).

[0013] The cracking furnace means of the method according to the invention can be any suitable thermal

cracking furnace known in the art. The various cracking furnaces are well known to those skilled in the art of cracking technology and the choice of a suitable cracking furnace for use in a cracking process is generally a matter of preference. Such cracking furnaces, however, are equipped with at least one cracking tube to which the hydrocarbon feedstock is charged or fed. The cracking tube provides for and defines a cracking zone contained within the cracking furnace. The cracking furnace is utilized to release the heat energy required to provide for the necessary cracking temperature within the cracking zone in order to induce the cracking reactions therein. Each cracking tube can have any geometry which suitably defines a volume in which cracking reactions can take place and, thus, will have an inside surface. The term "cracking temperature" as used herein is defined as being the temperature within the cracking zone defined by a cracking tube. The outside wall temperature of the cracking tube can, thus, be higher than the cracking temperature and possibly substantially higher due to heat transfer considerations. Typical pressures within the cracking zone will generally be in the range of from 0.135 to 0.273 MPa (5 psig to 25 psig) and, preferably from 0.170 to 0.239 MPa (10 psig to 20 psig).

[0014] As an optional feature of the invention, the hydrocarbon feed being charged to pyrolytic cracking furnace means can be intimately mixed with a diluent prior to entering pyrolytic cracking furnace means. This diluent can serve several positive functions, one of which includes providing desirable reaction conditions within pyrolytic cracking furnace means for producing the desired reactant end-products. The diluent does this by providing for a lower partial pressure of hydrocarbon feed fluid thereby enhancing the cracking reactions necessary for obtaining the desired olefin products while reducing the amount of undesirable reaction products such as hydrogen and methane. Also, the lower partial pressure resulting from the mixture of the diluent fluid helps in minimizing the amount of coke deposits that form on the furnace tubes. While any suitable diluent fluid that provides these benefits can be used, the preferred diluent fluid is steam.

[0015] The cracking reactions induced by pyrolytic cracking furnace means can take place at any suitable temperature that will provide the necessary cracking to the desirable end-products or the desired feed conversion. The actual cracking temperature utilized will depend upon the composition of the hydrocarbon feed stream and the desired feed conversion. Generally, the cracking temperature can range upwardly to 1093°C (2000°F) or greater depending upon the amount of cracking or conversion desired and the molecular weight of the feedstock being cracked. Preferably, however, the cracking temperature will be in the range of from 649 to 1038°C (1200°F to 1900°F). Most preferably, the cracking temperature can be in the range from 816 to 982°C (1500°F to 1800°F).

[0016] A cracked gas stream or cracked hydrocar-

bons or cracked hydrocarbon stream from pyrolytic cracking furnace means will generally be a mixture of hydrocarbons in the gaseous phase. This mixture of gaseous hydrocarbons can comprise not only the desirable olefin compounds, such as ethylene, propylene, butylene, and amylene; but, also, the cracked hydrocarbon stream can contain undesirable contaminating components, which include carbon monoxide.

[0017] It is generally observed that at the beginning or start of the charging of a feedstock to either a virgin cracking tube or a cracking tube that has freshly been regenerated by decoking, the concentration of undesirable carbon monoxide in the cracked hydrocarbon stream will be higher or reach a maximum concentration peak, which will herein be referred to as peak concentration. Once the carbon monoxide concentration in the cracked hydrocarbon stream reaches its peak or maximum concentration, over time it will gradually decrease in an almost asymptotic fashion to some reasonably uniform concentration. While the asymptotic concentration of carbon monoxide will often be sufficiently low to be within product specifications; often, the peak concentration will exceed specifications when there are no special efforts taken to prevent an excessive peak concentration of carbon monoxide. In untreated tubes, the peak concentration of carbon monoxide can exceed 9.0 weight percent of the cracked hydrocarbon stream. Conventionally treated tubes provide for a peak concentration in the range from 6 weight percent to 8.5 weight percent and an asymptotic concentration in the range of from 1 weight percent to 2 weight percent.

[0018] The cracker tube treatment method described herein provides for a reduced cumulative production of carbon monoxide in the cracked hydrocarbon stream during the use of such treated cracker tubes, and it provides for a lower peak concentration and asymptotic concentration of carbon monoxide. It has been found that the use of cracker tubes treated in accordance with the method described herein can result in a reduced peak concentration of carbon monoxide in a cracked hydrocarbon stream below that of conventionally treated tubes with the peak concentration being in the range of from 3 weight percent to 5 weight percent. The asymptotic concentration of carbon monoxide in a cracked hydrocarbon stream from cracker tubes treated in accordance with the method described herein also can be lower than that of conventionally treated tubes with such asymptotic concentration being less than 1 weight percent. In addition to preventing an off-spec olefin product, another advantage from having a lower carbon monoxide production in the cracking of hydrocarbons is that the hydrocarbons are not converted to carbon monoxide, but they are converted to the more desirable olefin end-products.

[0019] The invention includes treating the tubes of a cracking furnace by contacting such tubes with a reducing gas being hydrogen, containing a sulfur compound to thereby provide a treated tube. The sulfur compound

used in combination with the reducing gas to treat the cracking furnace tubes can be any suitable sulfur compound that provides for a treated tube having the desirable ability to inhibit the production of carbon monoxide when used in cracking operations.

[0020] Suitable sulfur compounds utilized include, for example, compounds selected from the group consisting of sulfide compounds and disulfide compounds. Preferably, the sulfide compounds are alkylsulfides with the alkyl substitution groups having from 1 to 6 carbon atoms, and the disulfide compounds are dialkylsulfides with the alkyl substitution groups having from 1 to 6 carbon atoms. The most preferred alkylsulfide and dialkylsulfide compounds are respectively dimethylsulfide and dimethyl disulfide.

[0021] The tubes treated with the reducing gas having a concentration of a sulfur compound will have the ability to inhibit the amount of carbon monoxide produced when used under cracking conditions. Also, both the peak concentration and the asymptotic concentration of carbon monoxide in the cracker effluent stream are reduced below those of a cracked effluent stream from untreated or conventionally treated cracker furnace tubes. Specifically, for the tubes treated with the reducing gas having a concentration of a sulfur compound, the peak concentration of carbon monoxide in the cracker effluent stream from such tube can be in the range of from 3 weight percent to 5 weight percent of the total effluent stream. The asymptotic concentration approaches less than 1 weight percent of the total effluent stream.

[0022] The tubes treated with the reducing gas containing a sulfur compound will have properties providing for a reduction in the production of carbon monoxide when used under cracking conditions below that of tubes treated with sulfur compounds but not in the presence of the reducing gas. It is preferred to contact the tubes under suitable treatment conditions with the reducing gas having a concentration of a sulfur compound. The reducing gas, which contains the sulfur compound, used to treat the cracker tubes is hydrogen gas. The concentration of the sulfur compound in the hydrogen gas used for treating the cracker tubes can be in the range of from 1 ppmw to 10,000 ppmw, preferably, from 10 ppmw to 1000 ppmw and, most preferably, from 20 to 200 ppmw.

[0023] The temperature conditions under which the reducing gas, having the concentration of the sulfur compound, is contacted with the cracking tubes can include a contacting temperature in the range upwardly to 1093°C (2000°F). In any event, the contacting temperature must be such that the surfaces of the cracker tubes are properly passivated and include a contacting temperature in the range of from 149 to 1093°C (300°F to 2000°F), preferably, from 204 to 982°C (400°F to 1800°F) and, most preferably, from 260 to 871°C (500°F to 1600°F).

[0024] The contacting pressure is not believed to be a critical process condition, but it can be in the range of

from atmospheric to 3.55 MPa (500 psig). Preferably, the contacting pressure can be in the range of from 0.170 to 2.17 MPa (10 psig to 300 psig) and, most preferably, 0.239 to 1.14 MPa (20 psig to 150 psig).

[0025] The reducing gas stream having a concentration of sulfur compound is contacted with or charged to the cracker tubes for a period of time sufficient to provide treated tubes, which when placed in cracking service, will provide for the reduced rate of carbon monoxide production relative to untreated tubes. Such time period for pretreating the cracker tubes is influenced by the specific geometry of the cracking furnace including its tubes; but, generally, the pretreating time period can range upwardly to 12 hours, and longer if required. But, preferably, the period of time for the pretreating can be in the range of from 0.1 hours to 12 hours and, most preferably, from 0.5 hours to 10 hours.

[0026] Once the tubes of a cracking furnace are treated in accordance with the procedure described herein, a hydrocarbon feedstock is charged to the inlet of such treated tubes. The tubes are maintained under cracking conditions so as to provide for a cracked product stream exiting the outlet of the treated tubes. The cracked product stream exiting the tubes which have been treated in accordance with the method according to the invention has a reduced concentration of carbon monoxide that is lower than the concentration of carbon monoxide in a cracked product stream exiting cracker tubes that have not been treated with a sulfur compound or that have been treated with a sulfur compound but not with the critical utilization of a reducing gas. As earlier described herein, the concentration of carbon monoxide in the cracked product stream from tubes treated in accordance with the method according to the invention can be less than 5.0 weight percent. Preferably, the carbon monoxide concentration is less than 3.0 weight percent and, most preferably, the carbon monoxide concentration is less than 2.0 weight percent.

[0027] Now referring to FIG. 1, there is illustrated by schematic representation a cracking furnace section 10 of a pyrolytic cracking process system. Cracking furnace section 10 includes pyrolytic cracking means or cracking furnace 12 for providing heat energy required for inducing the cracking of hydrocarbons. Cracking furnace 12 defines both convection zone 14 and radiant zone 16. Respectively within such zones are convection coils as tubes 18 and radiant coils as tubes 20.

[0028] A hydrocarbon feedstock is conducted to the inlet of convection tubes 18 by way of conduit 22, which is in fluid flow communication with convection tubes 18. Also, during the treatment of the tubes of cracking furnace 12, the mixture of hydrogen gas and sulfur compound can also be conducted to the inlet of convection tubes 18 through conduit 22. The feed passes through the tubes of cracking furnace 12 wherein it is heated to a cracking temperature in order to induce cracking or, in the situation where the tubes are undergoing treatment, to the required treatment temperature. The efflu-

ent from cracking furnace 12 passes downstream through conduit 24 where it is further processed. To provide for the heat energy necessary to operate cracking furnace 12, fuel gas is conveyed through conduit 26 to burners 28 of cracking furnace 12 whereby the fuel gas is burned and heat energy is released.

[0029] The following example is provided to further illustrate the present invention.

EXAMPLE

[0030] This example describes the experimental procedures used to treat a cracking tube and provides the results from such procedures. A comparative run and a run according to the invention were performed with the results being presented in FIG. 2.

[0031] A 3.66 m, 4.45 cm (12 foot, 1.75 inch) I.D. HP-Modified tube was pretreated with sulfur in the form of 500 ppmw dimethylsulfide for a period of three hours. Dimethylsulfide (DMS) was introduced with 12.0 kg/h (26.4 lb/hr) steam and 8.3 kg/h (18.3 lb/hr) nitrogen at 204°C (400°F) and 0.184 MPa (12 psig) several feet upstream of the electric furnace which enclosed the reactor tube. The average temperature in the reactor tube was 787.8°C (1450°F) during pretreatment. Ethane was then charged to the experimental unit at a rate of 11.5 kg/h (25.3 lb/hr), and steam was charged at a rate of 3.45 kg/h (7.6 lb/hr) while continuing to inject DMS at a concentration of 500 ppmw. Ethane conversion to ethylene was held constant at 67%. DMS injection was continued at 500 ppm for 9 hours into cracking, then was reduced to 125 ppm for the remainder of the run. Carbon monoxide production in the cracked gas, which is an indirect measure of the degree of coking, was monitored throughout the run.

[0032] In a subsequent run, the same tube was pretreated with a DMS/hydrogen mixture at a 1:1 (mole) ratio. The DMS concentration during pretreatment was 500 ppmw and all other conditions were the same during the pretreatment and during the cracking run. The carbon monoxide production in the cracked gas was monitored.

[0033] The carbon monoxide concentrations in the cracked gas for both of the runs are shown in FIG. 2. Carbon monoxide concentration showed a peak of 8.3 wt. % for the DMS only run while a peak of only 4.5 wt. % was obtained for the DMS/hydrogen run. The carbon monoxide concentration in the cracked gas remained higher in the DMS baseline run for several hours until the coke formed on the tube surface minimized reactions to carbon monoxide. These results clearly demonstrate the advantage of utilizing DMS in a reducing environment.

Claims

1. A method for reducing a concentration of carbon

monoxide present in a cracked gas stream produced by passing a hydrocarbon stream through a tube of a thermal cracking furnace, said method comprising:

treating said tube of said thermal cracking furnace by contacting said tube with a hydrogen gas containing a sulfur compound to thereby provide a treated tube having carbon monoxide production inhibiting properties; and

passing said hydrocarbon stream through said treated tube while maintaining said treated tube under suitable cracking conditions thereby producing said cracked gas stream having a reduced concentration of carbon monoxide below said concentration.

2. The method of claim 1, wherein said sulfur compound is dimethylsulfide.
3. The method of claim 1 or 2, wherein the concentration of said sulfur compound in said hydrogen gas is in the range of from 1 to 10,000 ppmw.
4. The method of any of claims 1 to 3, wherein said reduced concentration of carbon monoxide is such that the peak carbon monoxide concentration in said cracked gas stream is in the range of from 3 to 5 weight percent of said cracked gas stream.

Patentansprüche

1. Verfahren zur Verringerung einer Konzentration an Kohlenmonoxid, das in einem Crackgasstrom vorhanden ist, der durch Leiten eines Kohlenwasserstoffstromes durch ein Rohr eines thermischen Crackofens erzeugt wird, wobei das Verfahren aufweist:

Behandeln des Rohres des thermischen Crackofens durch In-Kontakt-Bringen des Rohres mit einem eine Schwefelverbindung enthaltenden Wasserstoffgas, um dadurch ein behandeltes Rohr mit die Erzeugung von Kohlenmonoxid hemmenden Eigenschaften zur Verfügung zu stellen; und

Leiten des Kohlenwasserstoffstromes durch das behandelte Rohr unter Halten des behandelten Rohres unter geeigneten Crackbedingungen, um dadurch den Crackgasstrom mit einer verringerten Konzentration an Kohlenmonoxid unterhalb der Konzentration zu erzeugen.

2. Verfahren nach Anspruch 1, wobei es sich bei der

Schwefelverbindung um Dimethylsulfid handelt.

3. Verfahren nach Anspruch 1 oder 2, wobei die Konzentration an der Schwefelverbindung in dem Wasserstoffgas im Bereich von 1 bis 10000 ppmv liegt. 5
4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die verringerte Konzentration an Kohlenmonoxid derart ist, dass die Peak-Kohlenmonoxid-Konzentration in dem Crackgasstrom im Bereich von 3 bis 5 Gew.-% des Crackgasstromes liegt. 10

Revendications

1. Un procédé pour réduire la concentration de monoxyde de carbone présent dans un courant de gaz craqué produit en faisant passer un courant d'hydrocarbures au travers d'un tube d'un four de craquage thermique, ledit procédé consistant à : 15

traiter ledit tube dudit four de craquage thermique en mettant en contact ledit tube avec de l'hydrogène gazeux renfermant un composé de soufre pour obtenir ainsi un tube traité ayant des propriétés d'inhibition de production de monoxyde de carbone et 25

faire passer ledit courant d'hydrocarbures au travers dudit tube traité tout en maintenant ledit tube traité sous des conditions de craquage appropriées produisant ainsi ledit courant de gaz craqué ayant une concentration réduite en monoxyde de carbone en-dessous de ladite concentration. 30
2. Le procédé selon la revendication 1, dans lequel ledit composé de soufre est du sulfure de diméthyle. 35
3. Le procédé selon la revendication 1 ou 2, dans lequel la concentration dudit composé de soufre dans ledit hydrogène gazeux se situe dans la gamme de 1 à 10000 ppm en poids. 40
4. Le procédé selon l'une quelconque des revendications 1 à 3, dans lequel ladite concentration réduite du monoxyde de carbone est telle que la concentration de monoxyde de carbone du pic dans ledit courant de gaz craqué se situe dans la gamme de 3 à 5% en poids dudit courant de gaz craqué. 45

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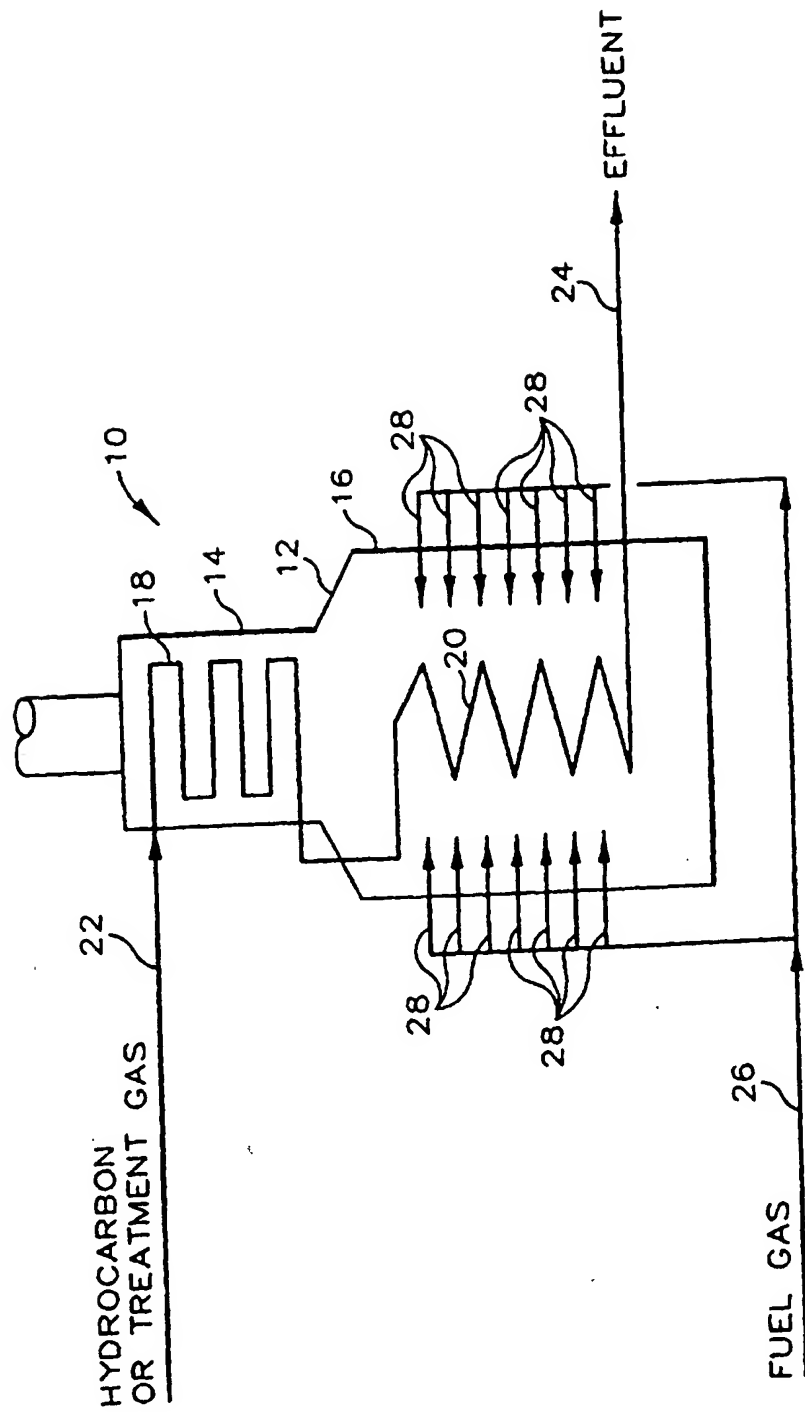


FIG. 1

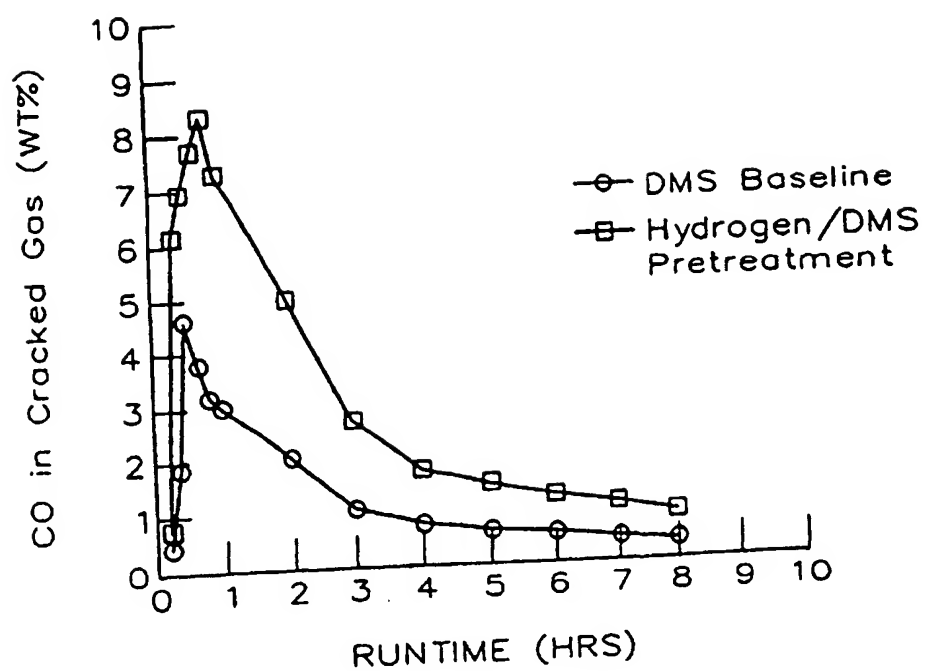


FIG. 2